

SCIENCE FOR GLASS PRODUCTION

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EFFECT OF COMPOSITION AND STRUCTURAL FACTORS ON THE VISCOSITY OF BOROSILICATE GLASSES AND MELTS

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The features of the effect of the composition and structure of glasses of the systems $\text{Na}_2\text{O} - \text{CaO} - \text{B}_2\text{O}_3 - \text{SiO}_2$ and $\text{Na}_2\text{O} - \text{CaO} - \text{B}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{SiO}_2$ on the temperature curve of the viscosity in the $10^{10} - 10^4 \text{ Pa} \cdot \text{sec}$ range were established. The important effect of phase separation processes — liquation and crystallization — on the viscosity indexes in the temperature region of the transition from the plastic to the liquid state was demonstrated.

Key words: borosilicate glass, structural factors, viscosity.

The analysis of the published data on investigation of the rheological properties of borosilicate glasses shows that in most cases, the viscosity is measured in the region of the vitrification temperatures (approximately $10^{12} \text{ Pa} \cdot \text{sec}$) due to the possibility of using different methods of measurement, including the dilatometric method. The viscosity in the temperature region of the transition from the plastic to the liquid state (so-called “temperature average viscosity”) was measured for separate compositions of borosilicate glass. The effect of metastable liquation, characteristic of glass systems of the $\text{R}_2\text{O} - \text{B}_2\text{O}_3 - \text{SiO}_2$ and $\text{RO} - \text{B}_2\text{O}_3 - \text{SiO}_2$ type, on the viscosity characteristics of glasses and melts was established [1, 2].

We determined the viscosity indexes in the range of dynamic viscosity coefficient values from 10^{10} to $10^4 \text{ Pa} \cdot \text{sec}$ (to 1000°C) on samples of glasses from the $\text{Na}_2\text{O} - \text{CaO} - \text{B}_2\text{O}_3 - \text{SiO}_2$ and $\text{Na}_2\text{O} - \text{CaO} - \text{B}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{SiO}_2$ systems, whose compositions are reported in Table 1. The glasses in these systems are the base in manufacturing many industrial compositions for glazes, enamels, glass fibers, optical glass, etc.

Determining the viscosity characteristics in the temperature region of the transition from the plastic to the liquid state is especially important in production of glass coatings made of borosilicate glass. In particular, glaze coatings are formed over a relatively long time (minimum of 1 h), which causes

evolution of phase separation processes at temperatures above the vitrification temperature. Formation of a liquation structure in heat treatment of borosilicate glasses significantly changes the viscosity indexes, especially in the skeleton type of liquation [1].

The mean temperature viscosity of the experimental glasses was measured on an Orton-PPV 1000 viscometer

TABLE 1. Experimental Glass Compositions

Composition	Molar oxide content, %				
	SiO_2	B_2O_3	Na_2O	CaO	Al_2O_3
1	75	10	10	5	—
2	65	20	10	5	—
3	65	10	20	5	—
4	65	10	10	15	—
5	65	10	10	5	10
6	70	15	10	5	—
7	70	10	15	5	—
8	70	10	10	10	—
9	70	10	10	5	5
10	65	15	15	5	—
11	65	15	10	10	—
12	65	15	10	5	5
13	65	10	15	10	—
14	65	10	15	5	5
15	65	10	10	10	5

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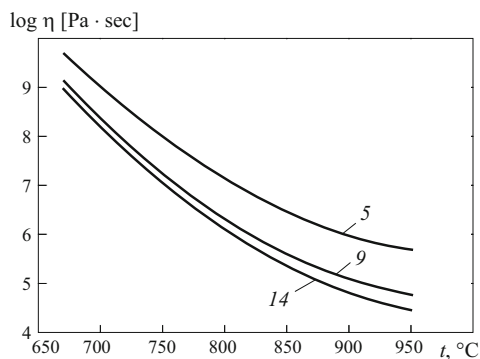


Fig. 1. Effect of Al_2O_3 on the temperature dependence of the viscosity of borosilicate glasses: the numbers on the curves correspond to the numbers of the glass compositions (see Table 1).

(USA). Samples in the form of small round bars 5 mm high were used for the experiment. The method of determining the viscosity with the deformation of the sample while heating under a load is the basis of operation of the instrument. The samples were rapidly heated to temperatures corresponding to the viscosity of 10^{10} Pa · sec, then the temperature elevation rate was reduced to 4–5 K/min.

An ÉM-125 transmitting electron microscope was used to study the structure of the experimental glasses and products of their heat treatment. The replica method with preliminary etching of the fresh surface area with 2% HF solution for 3–6 sec was used in preparation of the samples.

The temperature curve of the viscosity of glasses of the $\text{Na}_2\text{O} - \text{CaO} - \text{B}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{SiO}_2$ system with a 5–10%² Al_2O_3 content (here and below, the numbers of the curves on the temperature dependences of the viscosity correspond to the numbers of the glass compositions). The experimental data of the mean temperature viscosity are graphically a multitude of points. The dependence $\log \eta = f(t)$ is nonlinear. The polynomial line of a second-order trend (except for the samples in which crystallization occurred during the measurement) was selected as the approximating curve of the dependence of the mean temperature viscosity of the experimental glasses.

The viscosity of the aluminum-containing glasses monotonically decreased with an increase in the temperature. A 5% increase in the amount of Al_2O_3 due to SiO_2 increased the viscosity indexes by one order of magnitude on average, and the effect of aluminum oxide was more pronounced with an increase in the temperature. The high strength of the Al–O bond and formation and incorporation of $\text{AlO}_{4/2}\text{Na}$ groups in the silicon-oxygen skeleton decreased the degree of dissociation of the melt, manifested by a growing increase in the viscosity indexes in going from the plastic to the liquid state.

As Fig. 2 shows, the character of the temperature curve of the viscosity of the investigated glasses in the $\text{Na}_2\text{O} -$

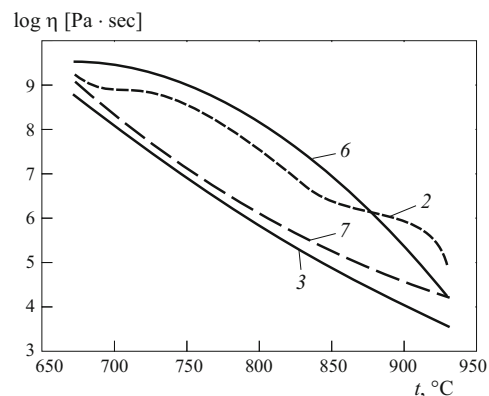


Fig. 2. Viscosity of glasses of the $\text{Na}_2\text{O} - \text{CaO} - \text{B}_2\text{O}_3 - \text{SiO}_2$ system with different $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ ratios: the numbers of the curves correspond to the numbers of the glass compositions (see Table 1).

$\text{CaO} - \text{B}_2\text{O}_3 - \text{SiO}_2$ system can change significantly as a function of the $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ ratio in them. The glass containing 20% Na_2O and 10% B_2O_3 (composition 3) had a gently sloping viscosity–temperature curve whose shape is characteristic of silicate glasses. At $\text{Na}_2\text{O}/\text{B}_2\text{O}_3 = 0.5$ (composition 2), the viscosity–temperature curve in the $10^{10} - 10^4$ Pa · sec range of values is more complex. The fact that the curve deviates from the typical curve of the viscosity of glass as a function of the temperature with an increase in the boron oxide content is confirmed by a comparison of the viscosity indexes of compositions 6 and 7. The viscosity of the glass containing 15% B_2O_3 decreased insignificantly in the 700–800°C temperature range, while it decreased sharply above 850°C. As a result, the viscosity of glasses with a different $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ ratio (at a constant SiO_2 content) differed significantly in the temperature region of the transition from the highly viscous plastic to the liquid state, but the viscosity indexes converged when the temperature was increased above 900°C. The temperature course of the viscosity of aluminum-containing samples did not exhibit such deviations in the character of the change in this index.

The features of the effect of boron oxide on the viscosity of glasses and melts are undoubtedly due to liquation phase separation, appearing in the stage of synthesis of borosilicate glasses and developing when the samples were heated during measurement.

According to the electron microscopic data, the initial experimental samples of the glasses had a microheterogeneous structure caused by metastable liquation. The samples of glasses from the $\text{Na}_2\text{O} - \text{CaO} - \text{B}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{SiO}_2$ system have a drop liquation structure with a drop size of 0.05–0.15 μm . The volume of the drop phase in the samples of the $\text{Na}_2\text{O} - \text{CaO} - \text{B}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{SiO}_2$ system increased with an increase in the boron and calcium oxide content. The size of the liquation inhomogeneities at a 20% B_2O_3 content (composition 2) was 0.25–0.4 μm , and up to 0.3 μm at a 15% CaO content (composition 4). Heat treatment of the samples at temperatures of 700, 800, 900, and 1000°C (heat-

² Here and below, mole fraction if not otherwise specified.

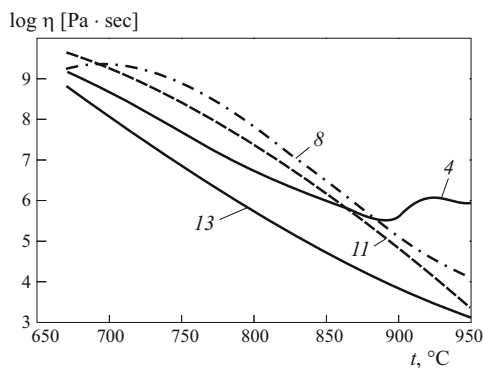


Fig. 3. Effect of CaO on the temperature curve of the viscosity of borosilicate glasses; the numbers of the curves correspond to the numbers of the glass compositions (see Table 1).

ing at the rate of 5 K/min, holding for 10 min) increased the size and number of microheterogeneities. The samples of composition 2 treated with heat at 900 and 1000°C exhibited the skeleton type of liquation.

A comparison of the data on the temperature dependences of the viscosity of the experimental glasses and their microstructure suggested that liquation phase separation affects the viscosity indexes at a high enough volume of drop phase (minimum of 30%), determined as both the size and the number of liquation inhomogeneities.

The viscosity indexes of the glasses containing B_2O_3 in the amount of 15 and 20% remaining at almost the same level when heated to 750°C indicates that the viscosity of the glass is on the whole determined by the highly viscous glass phase. The subsequent important decrease in the viscosity is not only due to an increase in the temperature, but also to the fact that the amount of SiO_2 decreases and the volume of glass phase enriched with boron oxide and modifier components also increases within the limits of the metastable liquation pot in the highly viscous phase. This causes the effect of the sodium and boron oxides on the viscosity to become equivalent at temperatures above 900°C and a constant SiO_2 content equal to 70%.

The break in the temperature curve of the viscosity at a 20% B_2O_3 content (composition 2) is probably due to the transition from the drop to the skeleton type of liquation. According to the data in [1, 2], in the skeleton (spinodal) type of liquation, the viscosity of the glasses is determined by the phase with the higher viscosity.

With an increase in the SiO_2 content due to B_2O_3 (composition 6), the volume of the drop phase becomes smaller, since phase separation processes evolve more slowly so that the viscosity of the liquating glass in the temperature range investigated decreases more monotonically and is probably determined by the viscosity of the glass phase enriched with silicon oxide.

The liquation structure of these samples is manifested in the entire temperature range of measurement (up to 1000°C), i.e., the liquation temperature is not attained. For this reason, the viscosity indexes were determined with the composition,

morphology, and ratio of the volumes of the glass phases, which in turn are a function of the composition of the initial glass, heat treatment temperature, and holding time. Correspondingly, a change in the heat treatment conditions will affect the viscosity indexes at temperatures below the liquation temperature. It was shown in [1] that the viscosity indexes of glasses of the $Na_2O - B_2O_3 - SiO_2$ system in the region of the vitrification temperature can increase by one order of magnitude and more with an increase in the holding time. However, the equilibrium compositions of the glass phases and correspondingly their viscosity indexes are attained more rapidly with an increase in the temperature.

In interpreting the data from the temperature dependence of the viscosity of borosilicate glasses in the region of the plastic and liquid state, it is necessary to consider a number of factors:

- the strength of the Me – O bonds, which decreases as the degree of their covalency decreases;

- the degree of polymerization of the structural groups; in the glasses investigated, the structural network can be formed by tetrahedral $SiO_{4/2}$, $Al_{4/2}Na$, $BO_{4/2}Na$, and $BO_{4/2}Ca_{0.5}$ groups;

- phase separation, primarily metastable liquation, and in many cases also crystallization.

The temperature curves of the viscosity of glasses of the $Na_2O - CaO - B_2O_3 - SiO_2$ system with a 5 – 15% CaO content are shown in Fig. 3. The viscosity indexes of glasses with a constant SiO_2 content equal to 65% differ significantly when Na_2O is substituted by CaO (compositions 13 and 4). There is an inflection in the experimental curve of the dependence of the viscosity of glass of composition 4 caused by an increase in the viscosity index in the temperature region above 900°C. The character of the viscosity curve of the glass of composition 1 containing the maximum amount of SiO_2 is similar in many of the investigated compositions (75%).

According to the electron microscopic data, in the 900 – 1000°C temperature range, together with metastable liquation, crystals 0.1 – 0.3 μm in size separate in the glass samples with the maximum SiO_2 (composition 1) and CaO (composition 4) content at heat treatment temperatures of 900 and 1000°C. The increase in the viscosity of the melts with an increase in the temperature is undoubtedly related to crystallization of the samples. The occurrence of crystallization processes on heating these samples is manifested on the viscosity temperature curves by an increase in the viscosity by 1 – 2 orders of magnitude in comparison to the uncrystallized samples. According to the data from gradient heat treatment, the samples are characterized by a higher tendency to crystallize in a number of the investigated compositions, manifested by formation of a crystalline crust. The less important increase in the viscosity of the crystallized samples is due to the low degree of crystallization. This is confirmed by the electron microscopic data, which show individual crystals in the samples heat treated at 900 and 1000°C.

Liquation phase separation of the drop type affects the character of the viscosity temperature curve of glasses with a calcium oxide content of 10–15%. This pertains to samples of compositions 8, 11, and 4 to the greatest degree. The difference in the shape of the temperature curves for compositions 11 and 13 is probably due to a change in the ratio of modifiers and boron oxide in them. In particular, equimolar substitution of B_2O_3 by Na_2O creates the grounds for transition of boron to four coordination in the composition of $BO_{4/2}Na$ groups and for a significant decrease in the proportion of three-coordination boron and as a consequence, a decrease in the tendency toward liquation separation.

Substitution of 5% CaO by Na_2O (compositions 8 and 13) significantly reduces the viscosity. This is not only due to a decrease in the strength of the bonds in the glass, but also to a decrease in the tendency toward liquation with an increase in the Na_2O content. Formation of a developed liquation structure increases the viscosity index due to separation of a glass phase enriched with SiO_2 .

The effect of liquation separation on the viscosity of glasses of the $Na_2O - CaO - B_2O_3 - SiO_2$ system does not allow evaluating the effect of the individual components. On the contrary, in aluminum-containing glasses containing drops less than $0.1 \mu m$ in size in the structure with a 5–10% drop phase volume, there is a tendency toward an increase in the viscosity with an increase in the B_2O_3 content, at the expense of Na_2O for a constant SiO_2 content (Fig. 4). At temperatures below $900^\circ C$, the quantitative viscosity indexes of the glasses are close, and in the $900 - 1000^\circ C$ range, substitution of Na_2O by B_2O_3 results in a more pronounced increase in the viscosity.

The features of the effect of the composition and structure of glasses of the $Na_2O - CaO - B_2O_3 - SiO_2$ and $Na_2O -$

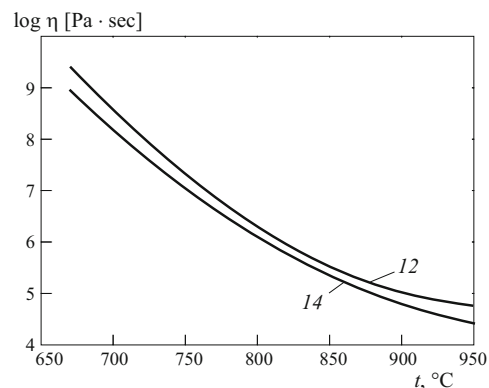


Fig. 4. Viscosity of aluminum-containing glasses with equimolar substitution of Na_2O by B_2O_3 ; the numbers of the curves correspond to the numbers of the glass compositions (see Table 1).

$CaO - B_2O_3 - Al_2O_3 - SiO_2$ systems on the viscosity indexes in the $10^{10} - 10^4 Pa \cdot sec$ range were thus established. The important effect of phase separation processes — liquation and crystallization — on the indexes of the mean temperature viscosity of glasses of the $Na_2O - CaO - B_2O_3 - SiO_2$ system was demonstrated. Formation of a liquation microstructure and separation of crystals during heat treatment of the experimental glasses increased the viscosity by 1–2 orders of magnitude and decreased the “length” of the glass.

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